Predicting Pesticide Transport in Mulch-Amended Soils: A Two-Compartment Model

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ABSTRACT

With adoption of combine harvest technology, massive sugarcane (*Saccharum* Spp. Hyb.) residue is left on the soil surface following each harvest, which could affect the environmental fate and efficacy of applied pesticides in subsequent cropping seasons. The objective of this study was to quantify the retention characteristics and mobility of a commonly used herbicide, atrazine (2-chloro-4-ethylamine-6-isopropylamino-S-triazine), in soils when sugarcane mulch residue was present. Specifically, adsorption and desorption kinetic batch experiments were performed to quantify atrazine retention by the mulch residue over time. Atrazine sorption exhibited time-dependent behavior and was followed by slow release regardless of input concentration. A kinetic—equilibrium model based on a second-order two-site (SOTS) formulation was successful in describing atrazine adsorption versus time by the mulch residue. One set of model parameters was capable of describing atrazine release based on six successive desorption steps. As a test for the applicability of the model, data sets from two other experiments where sorption and release was measured for extended time periods (1348 and 2476 h) were successfully predicted by the SOTS model. Miscible displacement methods were used to measure the mobility of atrazine in packed columns where the mulch residue was mixed with a reference sand material or a Sharkey clay soil (very fine, smectitic, thermic Chromic Epiaquerts). Use of batch-measured model parameters did not adequately describe atrazine mobility in the sand-mulch column. In contrast, for a Sharkey-mulch soil column, a two-compartment SOTS model was successful in predicting atrazine breakthrough results where independently estimated parameters for the mulch residue and the soil matrix were used as the input parameters. Results also showed that mixing of mulch with soil created physical non-equilibrium condition in the columns, which was responsible for errors in model predictions.

Since 1995, the sugarcane industry in Louisiana gradually adopted a new harvesting system that involves the use of a combine harvester that separates leaf-material from billets. The sugarcane residue is deposited directly on the soil surface and may intercept chemical spray and thus reduce the efficacy of soil-applied herbicide (Banks and Robinson, 1982; Ghadiri et al., 1984; Crutchfield et al., 1985). Atrazine remains a major herbicide that is used extensively in sugarcane production (Gianessi and Puffer, 1991). Chemical weed control programs for sugarcane usually require two herbicide applications, one before crop emergence and another post-emergence before the crop canopy closes. Sugarcane producers in southern Louisiana refer to the latter application as the layby treatment. Such herbicide treatments follow the last cultivation before harvest. Shading and competition from sugarcane plants usually control weeds developing after canopy closure. Atrazine is recommended as a pre-emergence treatment to control winter or early spring weeds or as a post-emergence treatment for layby or fallow fields.

The role of crop residue on the fate of applied agrichemicals in conservation tillage systems is not well understood. The effect of crop residue on interception, subsequent wash-off, and movement of herbicide in the soil profile is the primary focus associated with conservation measures in today's agriculture. Several conservation production systems are characterized by the presence of mulch residue left on the soil surface to protect it from water and soil erosion. In fact, several studies on best management practices (BMP) have shown distinct advantages of minimum or no-till systems (Dao, 1991, 1995; Banks and Robinson, 1982).

A literature search revealed that few studies have been performed on the fate and transport behavior of herbicides in the presence of mulch residue. One example was the column study by Dao (1991) where packed wheat straw was subjected to herbicide pulses under different velocities. Based on the shape of the breakthrough curves (BTCs), Dao (1991) concluded that metribuzin (4-amino-6-tert-butyl-4,5-dihydro-3-methyltio-1,2,4-triazin-5-one) was more retarded than S-ethyl-metribuzin. The strong affinity of wheat (*Triticum aestivum*) straw residue for metribuzin resulted in asymmetrical BTCs for all combinations of straw ages (straws collected at different times after harvesting). Breakthrough curves that exhibit asymmetry, which indicated slow herbicide release, were more pronounced at low pore-water velocities. In contrast to metribuzin retention based on batch sorption experiments by the wheat straw, significantly lower affinities of wheat straw for metribuzin during transport was observed. Such differences were attributed to possible chemical non-equilibrium conditions of the sorption-desorption processes during transport in the column experiments. Nevertheless, Dao (1991) concluded that the straw mulch is a temporary storage medium that alters herbicide retention patterns and may be a significant mechanism of retardation of the movement of applied agricultural chemicals to the subsurface under conservation tillage.

Field investigations on a Norge loam (fine-silty, mixed, active, thermic Udic Paleustolls) soil were later performed by Dao (1995) to determine the effect of placement of wheat straw on the mobility of metribuzin versus depth. Results of measured metribuzin concen-

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Abbreviations: BMP, best management practices; BTCs, breakthrough curves; CDE, the convective-dispersive equation; LSS, liquid scintillation spectroscopy; MRTM, multi-reaction transport model; RMSE, root mean square error; SOTS, second-order two-site.

tration in the soil profile revealed that standing residue or residue placed flat on the soil surface resulted in more metribuzin in the near surface zone compared with soils where the mulch was removed or moldboard plowed in. It was concluded that wheat residue intercepted metribuzin and attenuated subsurface mobility in no-till soils. In a field experiment with corn residue, Isensee and Sadeghi (1994) measured an average of 2.6 times more atrazine recovered in the top 10 cm of the soil under conventional till than under no-till. Moreover, the corn residue intercepted 60 to 70% of applied atrazine and 3 to 16% of the atrazine was recovered in the corn residue 1 to 2 wk later.

However, very few studies were conducted to correlate the effectiveness of sugarcane residue remaining on the soil surface on the retention of atrazine and its downward movement in the soil profile. Such information was a prerequisite in quantifying the role of the sugarcane residue in minimizing the leaching losses of applied agricultural chemicals. Recently, Selim et al. (2003) evaluated the effectiveness of sugarcane mulch residue on the retention of applied herbicides and their leaching losses in runoff. Based on the extractable amounts of herbicides measured, 1 wk following application, some 22% of the applied atrazine was retained by the mulch residue. They also found when the residue was not removed, a reduction in runoff-effluent concentrations, as much as 50%, for atrazine and pendimethalin was realized. Moreover, the presence of mulch residue resulted in consistently lower estimates for rates of decay or disappearance of atrazine and pendimethalin in the surface soil. In another study, Green et al. (1995) investigated the effect of corn residue, placed on the surface of undisturbed soil columns, on the transport of atrazine and chloride for different saturated hydraulic conductivities. They observed that atrazine recoveries based on leachate data were affected by the hydraulic conductivity (K_{sat}) of each column. The presence of mulch on the soil surface may have facilitated the mobility of chloride as well as atrazine in soil columns with high K_{sat} values, where double peaks for both chemicals were also observed. The occurrence of double peaks of atrazine is perhaps due to preferential flow or distinct dual porosity distributions. The effect of corn mulch on atrazine retention from the different columns was inconclusive, however.

Modeling the retention and mobility of herbicides by corn and wheat mulch residues was performed by several investigators. Such efforts were primarily focused on herbicide retention based on equilibrium Freundlich adsorption. For example, Dao (1991) measured the retention of wheat mulch for metribuzin and s-ethyl metribuzin from batch experiments and showed that the mulch exhibited a Freundlich type sorption behavior with values for the partitioning coefficients one to two orders of magnitude higher than soils. Dao (1995), as well as Green et al. (1995), used the convection-dispersion transport equation and quantified a retardation factor (R), which assumes equilibrium retention, to describe metribuzin and atrazine affinities based on field and laboratory transport experiments. From concentration distribution in the soil profile, measured R values varied from 3 to 4 when wheat residue was removed to R of 5 to 8 for soils with no-till wheat (Dao, 1995).

Kinetic adsorption models were not implemented in these previous efforts for describing the effect of mulch on the mobility of herbicides. Although the effect of kinetics on retention as well as slow release of herbicides in soils was investigated by a number of scientists, retention of herbicide by crop residues was described primarily by the Freundlich and/or Langmuir sorption of the equilibrium type models. Selim and Zhou (2005) used a two-site equilibrium-kinetic model of Selim et al. (1976) to describe pesticide retention in a series of batch experiments with sugarcane mulch and found that atrazine adsorption to sugarcane mulch was highly kinetic and the mulch had much higher adsorption capability than a loamy soil planted to sugarcane. In a later study, they also found that sugarcane mulch-amended soil delayed atrazine leaching in soil columns (Zhu, 2002). They also found that the Freundlich equilibrium model provided a poor description of the BTCs than the multi-reaction transport model (MRTM) of Selim et al. (1976). However, the study was limited to curve-fitting of the MRTM model because MRTM did not provide a means of deriving rate coefficients for the soil-mulch mixture from independently measured rate coefficients for soil and sugarcane mulch from batch experiments.

This study investigated the kinetics of atrazine sorption and release by sugarcane mulch residue and the subsequent influence on its mobility in soils. A SOTS equilibrium-kinetic approach was used where each constitute of the soil-mulch mixture had a maximum adsorption capacity and atrazine adsorption was a function of both atrazine concentration and available adsorption sites on the mixture. This model has proven to be successful in describing atrazine retention and transport in soils (Ma and Selim, 1994a, 1994b, 1996, 1998; Selim et al., 1999). The concept of a maximum adsorption capacity for atrazine has been used in the literature as well (Shelton et al., 1995). The second-order modeling approach also provides a means of estimating a maximum adsorption capacity for a mulch-soil mixture from individually measured adsorption capacities of soil and mulch. A number of batch and miscible displacement experiments designed to quantify atrazine interaction with the mulch residue and potential mobility in soils were performed. Objectives of this study were: (i) to quantify the adsorption-desorption characteristic of atrazine by sugarcane mulch residue using SOTS model; (ii) to extend the SOTS model to account for two compartments; namely the soil matrix and the mulch residue where each compartment has distinct herbicide retention characteristics; and (iii) to investigate the effect of sugarcane mulch residue on the transport of atrazine in mulch-amended soils using a two-compartment SOTS model.

MATERIALS AND METHODS

Sugarcane residue from first stubble (sugarcane variety: LCP85-384) was sampled from a private farm located about

8 km south of Baton Rouge, LA. Sampling was taken four months after combine harvest (16 Apr. 1999) but before spring application of herbicides. The mulch residue cover in the field was essentially 100% with mass, based on eight replications, of 4840 $\pm$ 423 kg ha^{-1}, and thickness of 5 cm. This site was chosen to evaluate several BMPs including no-till and to quantify the effect of mulch on herbicide retention and runoff losses (for details see Selim et al., 2003). The mulch residue used in our atrazine retention study was dried at 55°C for 24 h and then cut into 1-cm sections (in length) and stored at 5°C.

Sorption-Desorption

Atrazine sorption by the sugarcane mulch residue was performed using batch methods (Selim, 2003). Carbon-14-ring-labeled atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine] was obtained from Bayer Corp., Stillwell, KS, and diluted to 3×10^5 Bq mL $^{-1}$ as a tracer to monitor the extent of atrazine retention by the mulch residue. Specifically, six ^{14}C-atrazine spiked solutions having initial concentrations (C_i) of 3.37, 6.36, 12.34, 18.22, 24.30, and 30.16 μg mL^{-1} in 0.005 M $CaCl_2$ background solution were used. For adsorption, 30 mL of the various atrazine concentration solutions was added to 1 g of mulch residue in 40-mL Teflon centrifuge tubes in triplicate. The tubes were sealed with Teflon screw caps and placed on a reciprocal shaker. The mixtures were continuously shaken so that the mulch was in contact with atrazine solution at all times, and then centrifuged at 500 $\times$ g for 10 min for each specific reaction time before sampling. A 0.5-mL aliquot was sampled from the supernatant at reaction times of 2, 8, 24, 48, 96, 192, 288, and 504 h. The mixtures were returned to the shaker after each sampling. Amounts of ^{14}C-labeled atrazine in the supernatant were determined by mixing the 0.5-mL aliquot with 5 mL of scintillation fluid (Ultima-Gold-LS[1] cocktail, PerkinElmer, Wellesley, MA) and counted by liquid scintillation spectroscopy (LSS) (TRI-CARB TR2100, PerkinElmer Life and Analytical Sciences, Inc, Boston, MA). Amounts of atrazine sorbed on the mulch residue were determined by the difference between the concentrations of the supernatant and that of the initial solutions.

Desorption studies were conducted immediately following the last adsorption step (504 h) for all initial concentrations. Some 20 mL of supernatant solution was removed from the Teflon tubes and replaced with an equal amount of the 0.005 M $CaCl_2$ background solution. The exact volumes were evaluated by weighing. The mulch in the Teflon tubes was dispersed and then placed on reciprocal shaker for 24 at 23 $\pm$ 2°C. The tubes were then centrifuged for 10 min at 500 $\times$ g. Atrazine concentration in the supernatant solution during desorption was analyzed using LSS and the amount of atrazine desorbed from the mulch residue was calculated based on the change of atrazine concentration in solution (before and after desorption). The desorption process was repeated five more times for a total of six 24-h desorption steps. At the end of water extraction, sugarcane mulch was extracted with methanol.

In another adsorption-desorption experiment, hereafter referred to as batch Exp. II, the technique described above was followed except that only two initial (or input) atrazine concentrations (C_i) of 12.02 and 29.30 μg mL^{-1} were used. Atrazine solution was sampled with time up to 532 h. Five replications were used for each atrazine concentration. After 532 h of sorption, the supernatant in each tube was replaced with atrazine-free (0.005 M $CaCl_2$) solution (only once). The extent of release of atrazine from the sugarcane residue with time was subsequently sampled for a period of 816 h without changing the supernatant.

In a third batch experiment, hereafter referred to as batch Exp. III, we performed adsorption-desorption for initial concentrations (C_i) of 12.02 and 29.30 μg mL^{-1}, in a similar manner to that with batch Exp. II (five replications as well) with an important exception. Here we attempted to quantify the extent of atrazine retention or the capacity for sorption by the mulch residue. To achieve this, repeated replacements of the supernatants with respective (fresh) input atrazine solution were performed. Specifically, for each C_i, the supernatant was replaced with its respective atrazine solutions (about 30 mL) after each sampling time during adsorption. This was performed for the purpose of maintaining high atrazine concentrations in the solution phase during adsorption. These replacements occurred at the reaction times of 2, 8, 24, 72, 96, 192, 340, and 532 h. Immediately following adsorption (532 h), the supernatant was replaced with a atrazine-free solution once and atrazine in solution was sampled periodically as in batch Exp. II. After another 816 h, the supernatant was replaced with its corresponding atrazine solution to enforce a second adsorption for 192 h. After the second 192 h of adsorption, the supernatant was replaced again with atrazine-free solution and the amount of atrazine in solution was sampled for an additional 936 h. Total reaction time (adsorption and desorption) for this experiment was 2476 h.

Miscible Displacement

A series of miscible displacement column experiments were conducted by Zhu (2002) to investigate the effect of sugarcane mulch residue on atrazine retention in soils, including mulch and acid-washed sand mixture, mulch layer over a soil layer, and mulch-soil mixture. In this study, two column experiments were conducted to evaluate the SOTS model; one with mulch-sand mixture and one with mulch-Sharkey soil mixture. The columns were not repeated in this study. The reasons for using these two columns were that (i) mulch-soil mixture is a representation of soil tillage effect and the SOTS model can be easily applied to this uniform system than to a mulch/soil layered system and (ii) we have done extensive column studies with the same Sharkey soil using SOTS (Ma and Selim, 1994a, 1994b).

The two plexiglass columns (10 cm in length and 6.4 cm i.d.) were uniformly packed with either sugarcane mulch mixed reference sand or sugarcane mulch mixed Sharkey soil. The Sharkey soil was obtained from the St. Gabriel Research Station, Iberville Parish, LA, and was a common soil planted to sugarcane. It has the following properties: pH = 5.9, organic C = 1.41%, sand = 3%, silt = 36%, clay = 61%, cation exchange capacity (CEC) = 296 cmol$_c$ kg^{-1}, and dissolved organic carbon (DOC) = 2661.3 mg L^{-1}. Acid-washed sand was also used as a reference matrix where no clay or organic matter was present (pH = 6.27, sand = 81%, silt = 19, clay = 0%). Selim and Zhu (2002) used this sand material previously as a reference matrix in a deltamethrin transport (column) experiment and found this material was inert to the strong adsorptive deltamethrin. Therefore, adsorption of atrazine to the reference sand was not expected.

During packing of the soil column, the sugarcane mulch (1 cm in length) was incorporated into soil as uniformly as possible. For the sand column, the amount of mulch residue used was 14 g. For the Sharkey soil, the amount of mulch used was 11.7 g. Based on Zhu (2002), 4 g per 10-cm column was equivalent to average sugarcane mulch condition on the

[1] Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product by the authors, The Louisiana Agricultural Experiment Station or USDA.

Table 1. Soil properties and experimental conditions of individual columns of the miscible displacement experiments.

Column length	Material	Bulk density, ρ	Porosity, θ	Pore volume, PV	Darcy velocity, v	Dispersion coefficient, *D*	Atrazine pulse, PV
cm		g cm^{-3}	cm^3 cm^{-3}	cm^3	cm h^{-1}	cm^2 h^{-1}	
10	Reference sand-mulch	1.18	0.429	138.0	0.486	0.45†	7.09
10	Sharkey soil-mulch	0.966	0.538	173.0	0.405	3.80‡	9.78

† From Zhu (2002)
‡ From Ma and Selim (1994b).

soil surface after harvest. We packed much more mulch in each column to better show the flow interruption effects. Additional experimental and transport parameters for the various soil columns are listed in Table 1. Carbon-14-ring labeled atrazine was used as tracer as in the batch experiments. Atrazine BTCs were obtained by introducing atrazine pulses of various durations and followed by flow interruption and atrazine-free background water solution leaching.

Water saturation in each column was achieved by slowly introducing 0.005 *M* $CaCl_2$ solution where upward flow was maintained. Constant flux was controlled by a piston pump (FMI lab pump, Model QG 6, Fluid Metering Inc., Oyster Bay, NY). Following saturation, a pulse of ^{14}C-ring-labeled atrazine solution in 0.005 *M* $CaCl_2$ was introduced in each column. The volume of the pulse was 7.1 pore volumes (PV) for the sand-mulch column to 9.8 PV for the Sharkey-mulch column (Table 1). The atrazine pulses were followed by several pore volumes of 0.005 *M* $CaCl_2$ atrazine-free solution. For each column, two flow interruptions (4 d each) were performed: one during atrazine pulse (or adsorption) and one during leaching (or desorption), to assess the extent of physical and/or chemical nonequilibrium. Effluent samples from each column were collected using a fraction collector and atrazine concentrations in the effluent were subsequently analyzed using LSS by mixing a 0.5-mL sample with a 5-mL cocktail as described above.

Second-Order Model

This model is based on the assumption that adsorption affinities are different for the various constituents of the soil, and are represented by a system of consecutive and concurrent reactions. The model is capable of handling concurrent as well as the consecutive type solute interactions along the lines of surface diffusion, and inter- or intra-organic matter diffusion. Different sites with varied degree of affinity to solutes are analogs to concepts of solute retention via surface diffusion or intra-organic matter diffusion as discussed by Pignatello and Xing (1996), among others. A conceptual diagram of the general chemical non-equilibrium model is illustrated in Fig. 1, where C is solute concentration in soil solution (μg mL^{-1}), and S_e is the amount of solute retained by the soil matrix (μg g^{-1} soil) and is in equilibrium with C. The sorbed phase S_{irr} is a consecutive adsorption component from the kinetic site (S_k) and refers to irreversible adsorption sites (μg g^{-1} soil). The S_{irr} may also include degradation due to chemical and microbial activity. Associated parameters are as follows: K_e is the partitioning coefficient associated with equilibrium sites; k_1 and k_2 are the forward and backward reaction rate coefficients associated with the kinetic sites (S_k); and k_{irr} is the rate coefficient for the irreversible reaction, including irreversible adsorption and possible degradation. This model was successfully used to describe the retention and transport of atrazine (Ma and Selim, 1996; Ma and Selim, 1998) and metolachlor in soils (Selim et al., 1999).

Basic to the second-order formulation is that one assumes limited adsorption sites of solute on the soil, therefore, the reaction rates are functions of both solute concentration in solution and the availability of adsorption sites on the matrix (soil or mulch). Denoting ϕ as the amount of sites available for solute adsorption, the associated retention equations were (Selim et al., 1999):

$$S_e = K_e \theta C \phi \quad [1]$$

$$\frac{\partial S_k}{\partial t} = k_1 \theta C \phi - (k_2 + k_{irr}) S_k \quad [2]$$

$$\frac{\partial S_{irr}}{\partial t} = k_{irr} S_k \quad [3]$$

Here ϕ is related to the sorption capacity (S_{max}) by:

$$S_{max} = \phi + S_e + S_k \quad [4]$$

where ϕ and S_{max} are the unoccupied (or vacant) and total sorption sites on the matrix (soil or mulch), respectively (μg solute per g soil). In addition, S_{max} was considered as an intrinsic matrix property and is time invariant during the course of experiment. The unit for K_e is cm^3 μg^{-1}, k_1 is cm^3 μg^{-1} h^{-1}; and k_2 and k_{irr} are assigned with units of h^{-1}.

At equilibrium, total amounts of atrazine adsorbed on the S_e and S_k sites are:

$$S_T = S_e + S_k = S_{max}\left(\frac{\omega C}{1 + \psi C}\right) \quad [5]$$

Here $\omega = [(K_e + K_k)\theta]$ is the affinity coefficient of the combined equilibrium and kinetic adsorption, and $K_k = k_1/(k_2 + k_{irr})$. The mass balance equation for batch reactions is then written as:

$$-\theta \frac{dC}{dt} = \rho\left(\frac{dS_e}{dt} + \frac{dS_k}{dt}\right) \quad [6]$$

Subject to the appropriate initial and boundary conditions, the above system of Eq. [1] through [6] was solved using finite difference approximation methods (for details see Ma and Selim, 1994a and Selim et al., 1999).

Two-Compartment System

We now extend the above one-compartment SOTS formulation to a two-compartment system with each having a distict set of solute retention parameters, namely the soil matrix and the mulch residue. If one assumes that each compartment competes concurrently for the retention of solute present in the solution phase, S_{max} can be expressed as:

$$S_{max} = f[S_{max}]_r + (1 - f)[S_{max}]_m \quad [7]$$

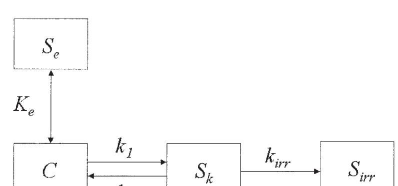

Fig. 1. A schematic diagram of the second-order two-site model.

where $[S_{max}]_r$ and $[S_{max}]_m$ represent the sorption capacity for the mulch residue and the soil, respectively. Here the dimensionless parameter f represents the fraction of the mulch residue in the soil-mulch mixture (on mass per unit bulk volume basis). This parameter is necessary to account for the proportion of each compartment per unit bulk volume of the soil. In Eq. [7] and subsequent equations, the subscripts r and m refer to the mulch residue and soil matrix, respectively.

Based on the second-order formulation, we can express S_{max} for each respective compartment as

$$[S_{max}]_r = [\phi]_r + [S_e]_r + [S_k]_r \quad [8]$$

$$[S_{max}]_m = [\phi]_m + [S_e]_m + [S_k]_m \quad [9]$$

Consequently, the amounts sorbed by the equilibrium sites of the mulch and the soils are

$$S_e = f[S_e]_r + (1 - f)\,[S_e]_m \quad [10]$$

Or more explicitly we have

$$S_e = \lambda\theta C \text{ where } \lambda = f[K_e]\phi_r + (1 - f)[K_e]_m\phi_m \quad [11]$$

Similarly, the amounts of atrazine adsorbed by the kinetic sites of both compartments are:

$$S_k = f[S_k]_r + (1 - f)\,[S_k]_m \quad [12]$$

where

$$\frac{\partial [S_k]_r}{\partial t} = [k_1]_r\theta C\phi_r - \{[k_2]_r + [k_{irr}]_r\}[S_k]_r \quad [13]$$

$$\frac{\partial [S_k]_m}{\partial t} = [k_1]_m\theta C\phi_m - \{[k_2]_m + [k_{irr}]_m\}[S_k]_m \quad [14]$$

In addition, the corresponding irreversible reactions are:

$$\frac{\partial [S_{irr}]_r}{\partial t} = [k_{irr}]_r\,[S_k]_r \quad \text{and} \quad \frac{\partial [S_{irr}]_m}{\partial t} = [k_{irr}]_m\,[S_k]_m \quad [15]$$

The above formulation was incorporated into the convective-dispersive equation (CDE) such that:

$$R\,\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} - v\,\frac{\partial C}{\partial X} - f\left(\frac{\rho}{\theta}\right)\frac{\partial [S_k]_r}{\partial t} - (1 - f)\left(\frac{\rho}{\theta}\right)\frac{\partial [S_k]_m}{\partial t} \quad [16]$$

and

$$R = 1 + \rho\lambda \quad [17]$$

The above CDE was solved subject to the following initial and boundary (third type) conditions (Selim et al., 1976):

$$C = 0 \qquad t = 0 \qquad 0 < x < L \quad [18]$$

$$S_e = S_k = S_{irr} = 0 \qquad t = 0 \qquad 0 < x < L \quad [19]$$

$$vC_o = -D\frac{\partial C}{\partial x} + vC \qquad x = 0 \qquad t \le t_p \quad [20]$$

$$0 = -D\frac{\partial C}{\partial x} + vC \qquad x = 0 \qquad t > t_p \quad [21]$$

$$\frac{\partial C}{\partial x} = 0 \qquad x = L \qquad t > 0 \quad [22]$$

where t_p is the duration of applied atrazine pulse (hour) and L is the column length (cm), C_o is the atrazine concentration in the applied pulse (μg mL^{-1}), and v is the pore velocity (cm h^{-1}). The CDE was solved numerically using the implicit-explicit finite difference approximation and is available from the authors.

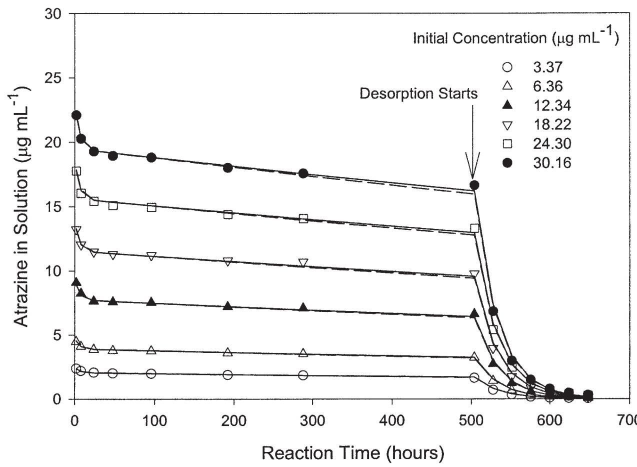

Fig. 2. Atrazine concentration in solution at various adsorption-desorption times in batch Exp. I. Solid lines are 'overall' fitted results and dash lines are predicted from averaged parameters of individually fitted adsorption-desorption curves for each initial concentration (see Table 2).

RESULTS AND DISCUSSION

Sorption-Desorption Kinetics

Decreases in atrazine concentration in solution versus reaction time for all the initial concentrations in batch Exp. I are illustrated in Fig. 2. Examination of the figure suggests that, for all initial concentrations (C_i), the adsorption of atrazine by sugarcane residue was initially rapid (about 80% of total adsorbed), and slowed down after 24 h. Continuous decrease in atrazine concentration was observed as the reaction time increased to 504 h. Although atrazine degradation was possible during the 504 h adsorption period, which was not measured in this study, it was unlikely to play any significant role during the batch experiment. Barriuso et al. (1997) observed no atrazine degradation in an organic compost for the first 30 d and about 10% degradation at the end of 250-d incubation at 28°C. Similar results were reported by Abdelhafid et al. (2000) and Moorman et al. (2001). Nonetheless, the contribution of degradation was accounted for by the S_{irr} site, which lumped degradation losses with irreversible sorption. However, atrazine disappearance from solution during the first 24 h was essentially due to adsorption alone. Therefore, the impact of degradation on sorption kinetics should be minimal.

Release of atrazine to solution at each desorption time is also shown in Fig. 2. After 6 d of desorption, 77 to 84% of input atrazine was recovered in water solution and additional 2 to 3% was recovered in methanol solution. The rest was either non-extractable or degraded (Selim and Zhu, 2005).

To utilize the SOTS model in describing atrazine retention kinetics, it was necessary to estimate the maximum adsorption capacity parameter (S_{max}) for the mulch residue. To achieve this, we followed the method described earlier by Ma and Selim (1994a). First we re-

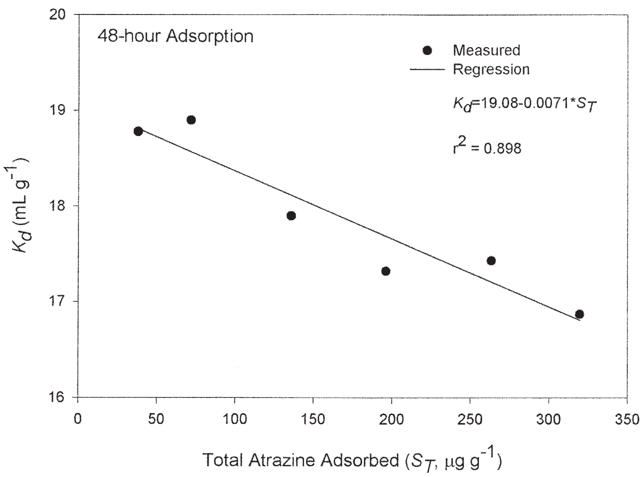

Fig. 3. Total atrazine adsorbed by sugarcane residue vs. distribution coefficient (K_d) for estimating maximum adsorption capacity (S_{max}).

arranged the Langmiur Eq. [5] into the following linearized form,

$$K_d = \frac{S_T}{C} = \omega S_{max} - \omega S_T \qquad [23]$$

where K_d is a commonly used distribution coefficient (mL g^{-1}) for describing adsorption isotherms. We plotted K_d versus the total amount of atrazine sorbed (S_T) for each reaction time. Highest regression coefficient (r^2) was obtained for a 48-h reaction time. The K_d versus S_T regression equation and related statistics shown in Fig. 3 provided an estimate of S_{max} of 2681 µg g^{-1} for the mulch residue. We are not aware of values for atrazine sorption capacity for sugarcane mulch residue. As will be discussed in subsequent sections, based on our third batch experiment, the highest experimentally measured S_{max} for atrazine was 763 µg g^{-1}, which is considerably lower than our estimated S_{max} value. Shelton et al. (1995) reported a laboratory measured atrazine sorption capacity for dried and ground cornstalk of 860 µg g^{-1}. Therefore, our estimated S_{max} value of 2681 µg g^{-1} for the mulch represents potential adsorption at large times ($t \rightarrow \infty$) when adequate supply of atrazine in solution C is maintained using the Langmiur equation.

The goodness-of-fit of the SOTS model was tested using our sorption-desorption data set for all initial concentrations. Second-order two-site model parameter estimates given in Table 2 were obtained using nonlinear least square optimization for each initial atrazine concentration C_i (3.37, 6.36, 12.34, 18.22, 24.30, and 30.16 µg mL^{-1}). We also obtained an "overall' set of model parameters (Table 2) where the entire data set for all C_i's were used in the nonlinear least-square parameter estimation procedure. Model calculations as shown by the solid and dashed curves in Fig. 2, clearly illustrate the capability of the model in describing our batch results. Based on the goodness-of-fit and their statistics, sorption as well as desorption results were well described by the SOTS model as illustrated by the low parameter standard errors and high r^2s. The use of a simple arithmetic average of parameter estimates of all six initial concentrations yielded a set of parameter values that were reasonably close to those based on the "overall" parameters (see Table 2). When we used the arithmetic average parameters, we obtained a value for root mean square error (RMSE) of 0.174 µg mL^{-1}, which was not significantly different from that based on the "overall" set of parameters ($RMSE$ = 0.164 µg mL^{-1}). It should note that only one set of parameter values was needed to describe the retention for the entire concentration range. In other words, these parameters were independent of initial atrazine concentrations. It is also of interest that the calculated ω [$= (K_e + K_k)\theta$ with $\theta \approx 1.0$] values from both "overall fitting" and average k values were 0.0066, which is close to the 0.0071 value obtained from Eq. [23] (Fig. 3).

The parameters from "overall" fitting were used thereafter to predict atrazine adsorption-desorption from batch Exp. II and III as well as the column transport studies. After 532 h of sorption, the supernatant in each tube was replaced with atrazine-free (0.005 M $CaCl_2$) solution (only once). The extent of release of atrazine from the sugarcane residue with time was subsequently sampled for a period of 816 h without replacing the supernatant. The measured and modeled atrazine concentrations in solution from batch Exp. II, Fig. 4, indicated that the SOTS model well predicted the changes in atrazine concentrations during sorption as well as during release following the desorption step. The RMSE of the model was 0.273 µg mL^{-1}.

The SOTS model was further tested to predict atrazine sorption-desorption in batch Exp. III, where two sorption-desorption cycles were implemented. The model was used in a predictive mode with parameters from the overall fitting given in Table 2. As illustrated in Fig. 5, model predictions described the measured atrazine concentrations. These predictions illustrate the versatility as well as the capability of the SOTS model to handle various sorption and desorption scenarios over time. We are not aware of other models that are capable

Table 2. Fitted model parameters from adsorption-desorption study of sugarcane mulch Exp. I along with their standard error (SE) and root-mean square error (RMSE) for different initial concentrations (C_i's).

C_i	r^2	RMSE	K_e	SE	k_1	SE	k_2	SE	k_{irr}	SE
µg mL^{-1}		µg mL^{-1}	(µg/mL)$^{-1}$		— (µg/mL)$^{-1}$ h^{-1} —		h^{-1}		h^{-1}	
3.37	0.999	0.03099	0.003648	0.000352	0.000378	0.000133	0.134197	0.039111	0.002982	0.000456
6.36	0.999	0.05654	0.003824	0.000350	0.000369	0.000132	0.127987	0.037166	0.002351	0.000364
12.34	0.999	0.12627	0.003195	0.000384	0.000424	0.000143	0.125374	0.034265	0.001768	0.000290
18.22	0.999	0.19195	0.003340	0.000526	0.000523	0.000247	0.171827	0.061166	0.002070	0.000415
24.30	0.999	0.23473	0.003275	0.000489	0.000580	0.000224	0.168432	0.049734	0.001759	0.000310
30.16	0.999	0.28279	0.003519	0.000419	0.000435	0.000167	0.138472	0.042118	0.001940	0.000332
Average	0.999	0.17454	0.003467		0.000452		0.144382		0.002145	
Overall fitting	0.999	0.16420	0.003507	0.000154	0.000472	0.000068	0.151549	0.017451	0.001974	0.000128

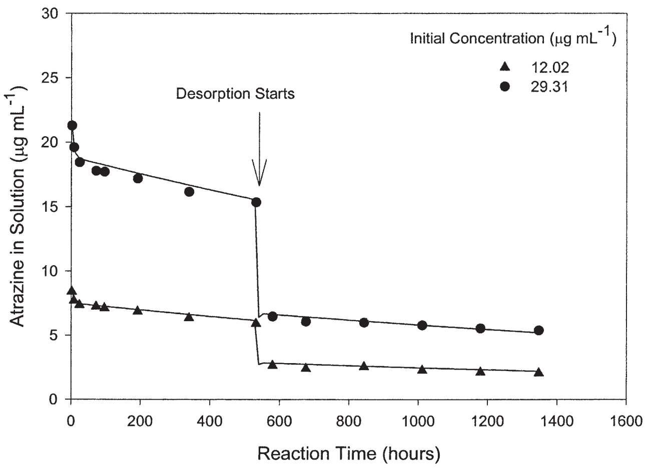

Fig. 4. Atrazine concentration in solution at various adsorption-desorption times in batch Exp. II.

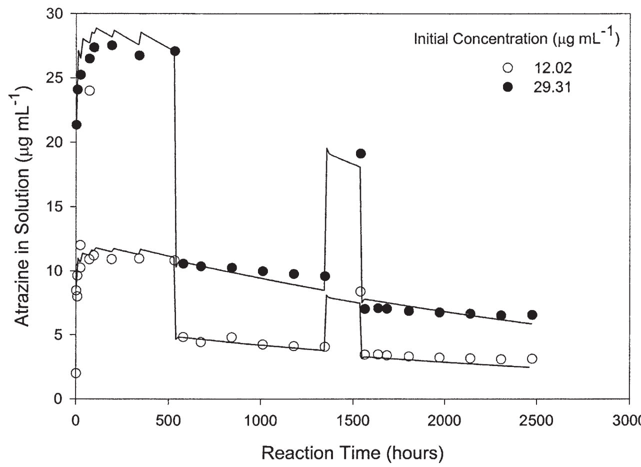

Fig. 5. Atrazine concentration in solution at various adsorption-desorption times in batch Exp. III.

of predicting sorption and desorption kinetics where only one-set of model parameters is used.

Transport Experiments

To predict atrazine transport in columns, it was necessary to know physical parameters such as ρ, θ, the water flux density (v), and the hydrodynamic dispersion coefficient D, in addition to all the SOTS model parameters (e.g., S_{max}, K_e, k_1, k_2, k_{irr}). A dispersion coefficient (D) of 0.45 cm^2 h^{-1} was obtained from Zhu (2002) based on a similar sand-mulch column and a D of 3.80 cm^2 h^{-1} was used for the Sharkey-mulch column from Ma and Selim (1994b). An estimate for S_{max} of 98.77 μg g^{-1} for the sand-mulch column was based on the amount of mulch incorporated into each column assuming that the sand material was inert and atrazine could only be retained by the mulch residue. For the Sharkey-mulch column, we estimated S_{max} of 278.83 μg g^{-1} by using a previously measured value of S_{max} of 184.62 μg g^{-1} for the Sharkey soil based on the work of Ma and Selim (1994a). Therefore, the contributions of the mulch and Sharkey soil to the sorptive capacity accounted for 101.20 and 177.63 μg g^{-1}, respectively, which represents 36% (i.e., f = 0.36) and 64% of the total S_{max} in Sharkey-mulch column. In addition, the respective values of retention parameters (K_e, k_1, k_2, and k_{irr}) for atrazine sorption in Sharkey soil were also obtained from Ma and Selim (1994a) and are listed in Table 3.

Sugarcane mulch caused delay in atrazine breakthrough and extensive tailing of the measured BTC from the sand-mulch column, compared with a simulated BTC using the SOTS model with ρ = 1.67 for a hypothetical sand column under the same experimental conditions (Ma and Selim, 1994c, Fig. 6). Maximum peak concentration was also lower than the hypothetical sand column. Some 3.1 pore volumes (V/V_o) were needed to reach relative concentration of 0.5 (C/C_o). Very little response to the first flow interruption at pore volume of 3.1 was observed, whereas a reasonable jump in atrazine leachate solution was observed for the second flow interruption at 9.5 pore volumes. A response to flow interruption is indicative of non-equilibrium behavior during transport caused by chemical and/or physical processes, for example, interparticle diffusion and kinetic retention (Murali and Aylmore, 1980; Reedy et al., 1996). Predicted atrazine BTC for the sand-mulch column using the batch-derived parameters is shown by the dashed curve of Fig. 6. The model overpredicted peak concentration and the front portion of the BTC and underpredicted the tailing portion of the BTC with RMSE of 0.260 μg mL^{-1} (Fig. 6). However, simulation results were improved when S_{max} alone (= 355.9 μg g^{-1}) was adjusted to fit the BTC as shown by the dotted curve of Fig. 6 where the overall RMSE was reduced to 0.085 μg mL^{-1}. The fitted S_{max} was some three orders of magnitude higher than that based on mulch weight and batch-measured S_{max} (Table 3). Such a value for S_{max} is unrealistic and the adjustment of S_{max} is, therefore, not recommended. In contrast, when the retention parameters alone (K_e, k_1, k_2, and k_{irr}) were optimized using batch derived S_{max}, the SOTS model provided extremely good prediction of the overall BTC as illustrated by the solid curve in Fig. 6 where lowest RMSE value of 0.053 μg mL^{-1} was attained. The associated best-fit parameters, which lumped the physical non-equilibrium effect into them, indicated that the contribution of kinetic retention was dominant (see Table 3). Also, constant shaking during batch experiments might have made kinetics less important than under column flow conditions. Although model calculations provided some response to the change in concentration due to flow interruption, the model failed to adequately describe the big increase in atrazine concentration during the second flow interruption (see Fig. 6). It was possible that physical non-equilibrium played an important role during the second flow interruption, which was not considered in the current model.

It was interesting to observe that with sugarcane mulch incorporated, atrazine BTC from the Sharkey-mulch column showed early breakthrough and less tailing than a simulated BTC for a hypothetical Sharkey soil column under the same condition using the SOTS model with ρ = 1.19 (Ma and Selim, 1994a, 1994b) (Fig. 7). Such behavior suggested that mulch residue caused physical non-equilibrium in the Sharkey-mulch

Table 3. Model parameters that provided best-fit for the atrazine breakthrough curves (BTC's) for the sand-mulch column along with parameters used for Sharkey-mulch column. Root mean square errors (RMSE) and coefficient for correlation (r^2) are given for the predicted BTC's shown in Fig. 6 and 7.

Model parameter	Sand-mulch (fitted)	Sharkey-mulch (fitted)	Sharkey-mulch† (weighted average)	Sugarcane-mulch (from Table 2)	Sharkey‡
K_e (μg/mL)$^{-1}$	0.002720	0.008118	0.011528	0.003507	0.016040
k_1 (μg/mL)$^{-1}$ h^{-1}	0.001601	0.000077	0.000238	0.000472	0.000107
k_2 (h^{-1})	0.046725	0.015800	0.060615	0.151549	0.009465
k_{irr} (h^{-1})	0.018638	0.005685	0.001753	0.001974	0.001628
RMSE (μg mL^{-1})	0.053	0.052	0.104		
r^2	0.997	0.971	0.897		

† Model parameter values are based on weighted average parameters from independently measured mulch parameters (overall fitting in Table 2) and Sharkey parameters (Ma and Selim, 1994a, see text).
‡ Model parameter values are for Sharkey soil obtained from Ma and Selim (1994a).

column. This is in agreement with Green et al. (1995). Physical non-equilibrium might be due to possible preferential flow paths around the formed network by sugarcane mulch in the column or due to different water affinities between mulch and soil. Flow interruptions at pore volumes of 6.5 and 13.0 caused observable change in atrazine concentration, which was indicative of non-equilibrium behavior for atrazine in Sharkey soil. Predictions of atrazine BTC using the two-compartment SOTS model for the Sharkey-mulch column shown in Fig. 7 were considerably better than those for the sand-mulch column. The use of experimentally measured retention parameters for the sugarcane mulch residue, as well as for the Sharkey soil, yielded a model prediction that was reasonable with RMSE of 0.096 μg mL^{-1}. The model well predicted the peak position of the BTC but slightly under-predicted the concentration maxima (see Fig. 7). The tailing portion was somewhat over predicted. The model was only capable of responding to the first interruption event during sorption (Fig. 7). It was conceivable that physical, instead of chemical, non-equilibrium was responsible for such behavior during atrazine release. Pignatello and Xing (1996) postulated that slow release was due to retention via surface diffusion or intra-organic matter diffusion. Selim et al. (1999) described BTCs for metolachlor in Sharkey soil having different size aggregates. They concluded that flow interruptions for metolachlor were better described when physical non-equilibrium, based on the mobile-immobile concept, was incorporated into the SOTS model. The almost perfect match between simulated results from the two-compartment model and the hypothetical Sharkey soil column further showed that the contribution of sugarcane mulch to atrazine BTC was minimal in terms of chemical non-equilibrium. Sugarcane mulch might contribute more to physical non-equilibrium in the Sharkey-mulch column.

We further tested the one-compartment SOTS model to find out whether the weighted average parameters from mulch and Sharkey soil were adequate in simulating atrazine BTC, since the incorporated mulch would become part of the soil when decayed. Here the set of model parameters were "weighted averages" of the rate coefficients and were derived based on their respective

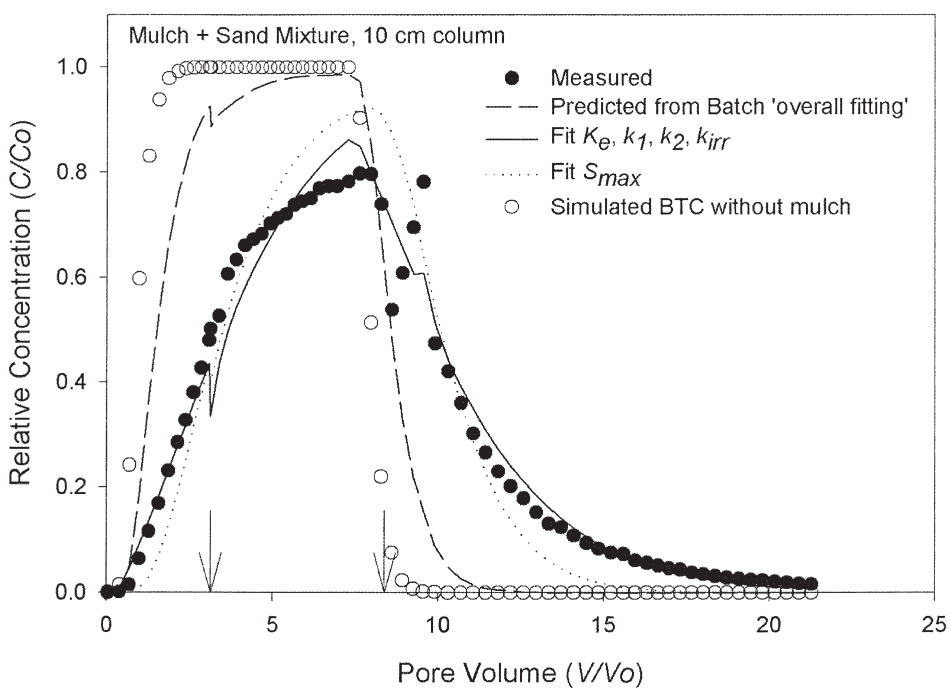

Fig. 6. Measured and simulated atrazine breakthrough curves (BTCs) from the sand + mulch column. Arrows indicate pore volumes when flow interruptions occurred.

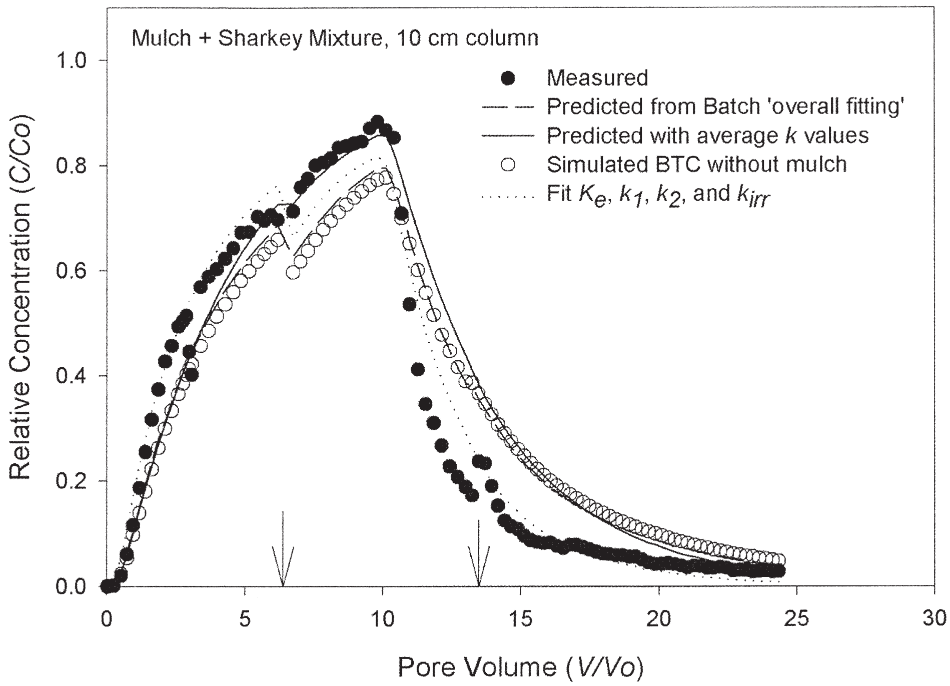

Fig. 7. Measured and simulated atrazine breakthrough curves (BTCs) from the Sharkey + mulch column. Arrows indicate pore volumes when flow interruptions occurred.

contributions of the mulch (36%) and Sharkey soil (64%) to total adsorption sites (Table 3). The resulting model calculations, shown as solid curve in Fig. 7, may be regarded as adequate prediction of atrazine behavior in our Sharkey-mulch column. Therefore, the use of weighted retention parameter values for atrazine into the SOTS model is conceivable. We did not adjust the value for the capacity term S_{max}, because adjusting S_{max} did not improve simulation results considerably. An attempt was made to utilize nonlinear optimization to improve model description of the BTC from the Sharkey-mulch column by fitting the weighted average k values (K_e, k_1, k_2, and k_{irr}) using the one-compartment model (Table 3). Although the curve-fitting exercise improved simulated BTC, it failed to account for the jump in concentration during the second flow interruption. Therefore, physical non-equilibrium was still partially responsible for the measured atrazine BTC in the Sharkey-mulch column (Fig. 7).

CONCLUSIONS

We measured atrazine retention (sorption-desorption) by sugarcane mulch residue for a wide range of concentrations and reaction times using kinetic batch methods. Both sorption as well as desorption of atrazine by the mulch residue were time-dependent in nature. The use of a SOTS (equilibrium-kinetic) model was successful in describing adsorption results for the entire concentration range. Moreover, one set of model parameters from the entire data set, including both adsorption and desorption for an entire range of initial input concentrations, were adequate in describing the batch results. Furthermore, when the model was used in a predictive mode, where all rate coefficients for atrazine retention were provided as inputs, results from other batch experiments where sorption and release were measured for extended time periods, were successfully predicted by the SOTS model. We concluded that one set of model parameters provided good predictions of atrazine retention by the mulch residue. We also found that rate coefficients based on a simple average of parameter estimates from individually fitted adsorption-desorption curves for each initial atrazine concentration provided equally good prediction compared with "overall" rate coefficients.

To assess the influence of the mulch residue on the mobility of atrazine, miscible displacement methods were used with packed columns where the mulch residue was mixed with a reference sand material or a Sharkey clay soil. For reference sand column, the use of independent set of parameters from our batch experiments did not adequately describe atrazine mobility in the sand columns. In contrast, for the Sharkey soil column, a two-compartment SOTS model was successful in predicting atrazine breakthrough results where two sets of parameters from the mulch residue and the soil matrix were used as the input parameters. Simulation results also suggested that sugarcane mulch created physical non-equilibrium in the Sharkey-mulch columns. Therefore, when sugarcane residue is mixed in the soil profile by tillage, atrazine transport in the soil profile may be expedited by preferential flow and models accounting for physical non-equilibrium are needed.

Future research should account for decomposition of the sugarcane mulch residue as well as changes in herbicide retention characteristics due to weather-induced changes following harvest. The contribution of pesticide degradation in the presence of sugarcane mulch needs to be studied. Attempts should be made to extend the SOTS model to incorporate temporal changes in herbicide retention parameters as well as the mass of residue with time following harvest. It is also of practically important to enhance the SOTS model to simulate mulch and soil layered system for no-till conditions.

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